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# THE UNITED STATES OF AMERICA

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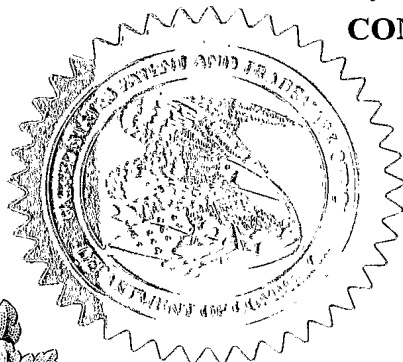
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By Authority of the  
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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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**INVENTOR(S)**

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John P.	Rosini	Seabrook, Texas

Additional inventors are being named on the \_\_\_\_\_ separately numbered sheets attached hereto

**TITLE OF THE INVENTION (500 characters max)**

POLYMERIZATION INITIATOR SYSTEMS CONTAINING ALUMINUM COMPOUNDS AS CURING INHIBITORS AND POLYM

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**ENCLOSED APPLICATION PARTS (check all that apply)**

<input checked="" type="checkbox"/> Specification Number of Pages <u>7</u>	<input type="checkbox"/> CD(s), Number _____
<input type="checkbox"/> Drawing(s) Number of Sheets _____	<input type="checkbox"/> Other (specify) _____
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76	

**METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT**

<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.	<b>FILING FEE Amount (\$)</b>  160.00
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

<input checked="" type="checkbox"/> No.
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____

[Page 1 of 2]

Respectfully submitted,

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Date March 1, 2004

REGISTRATION NO. 25,677

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**POLYMERIZATION INITIATOR SYSTEMS CONTAINING ALUMINUM COMPOUNDS AS  
CURING INHIBITORS AND POLYMERIZABLE COMPOSITIONS MADE THEREWITH**

**Background of the Invention**

5       The present invention relates to a novel curing inhibitor  
for amine organoborane complex polymerization initiators of the  
type described and claimed in U.S. Patent Application Publication  
No. 2002/0058764, the references described therein to Mottus et  
al., Skoultchi, Zharov et al., and Pocius, in the following  
10   related U.S. Patent Application Publication Nos. 2002/0025381,  
2002/0028894, 2002/0031607, 2002/0033227, and 2003/0120005, and  
in the original U.S. Patent Application No. 09/466,321. All of  
these patent applications and patents are incorporated herein by  
reference as covering the amine organoborane complex  
15   polymerization initiators that are useful in the practice of the  
present invention. As stated in at in paragraphs 0002 and 0009  
of U.S. Patent Application Publication No. 2002/0058764, it is  
desired to have polymerization initiator systems that have  
enhanced stability in the presence of compounds having olefinic  
20   unsaturation, thus improving the ability to cure on demand.

**Summary of the Invention**

One embodiment of the present invention is a composition  
comprising an organoborane/amine complex and an effective amount  
25   of an aluminum compound to inhibit curing of the  
organoborane/amine complex when used as part of a polymerization  
initiator system containing one or more monomers, oligomers or  
polymers having olefinic unsaturation. Paragraph 0010 of U.S.  
Patent Application Publication No. 2002/0058764 provides a non-  
30   limiting but representative description of organoborane and amine  
components that can be selected for use. The embodiments listed

in paragraphs 0011 and 0012 of this same patent publication are relevant to the use of this composition, and the statements made in paragraph 0013 regarding the characteristics of the composition also hold true for the composition of the present invention.

#### Description of Preferred Embodiments

Paragraph 0014 and the first seven lines of paragraph 0015 of U.S. Patent Application Publication No. 2002/0058764 describe the organoborane used in the complex while paragraphs 0017 to 0044 also describe certain amines that can be selected for use in the practice of the present invention. Other amines can also be used (for example, as described in U.S. Patent No. 5,935,711 in Cols. 5 to 8).

A variety of organoaluminum compounds of the formula  $Al_2R_6$  can be selected for use in the present invention. In the preceding formula R is either  $C_1$ - $C_{12}$  alkyl or  $C_1$ - $C_{12}$  alkoxy, with each of the six R groups being the same or different. By extension, this formula also represents compounds explicitly designated as  $AlR_3$  and  $Al(R)(R')_2$  for compounds of the formula with even numbers of alkyl and/or alkoxy groups. The R groups can be a mixture of about three alkyl groups and about three alkoxy groups. The terms "alkyl" and "alkoxy" as used herein includes both straight-chain and branched-chain groups.

Non-limiting examples of organoaluminum compounds within the scope of this invention include trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, aluminum triethoxide, aluminum isopropoxide, aluminum tri-s-butoxide, aluminum tri-t-butoxide, diethylaluminum ethoxide,

diisobutylaluminum ethoxide, triethyl(tri-s-butoxy)dialuminum, tri-n-butyl(triisopropoxy)dialuminum, and mixtures thereof.

The organoaluminum compound can either be added directly to the organoborane prior to reaction with amine to prepare the organoborane/amine complex or it can be added directly to the  
5    prepared organoborane/amine complex.

The molar ratio of boron to aluminum in the composition is relatively important. If the molar ratio of boron to aluminum is too high, then the polymerizable composition made therewith may  
10    experience an undesirable increase in viscosity. If the molar ratio of boron to aluminum is too low, the composition may be pyrophoric (the absolute ratio at which the composition is pyrophoric is dependent upon the organoaluminum compound that is used) or there may be problems with adhesion. The molar ratio of  
15    boron to aluminum can range from about 1.0:1.0 to about 50.0:1.0. Within this described range, for example, the molar ratio of boron to aluminum can range from about 10.0:1.0 to about 30.0:1.0.

U.S. Patent Application Publication No. 2002/0058764  
20    describes the organoborane/amine complex (at paragraph 0045), the polymerizable compounds and compositions (at Paragraphs 0046 to 0048), the preparation and properties of the organoborane/amine complex (at paragraphs 0049 to 0051) and the applications of the polymerizable compositions (at paragraphs 0052 to 0071 and 0073  
25    to 0075). Paragraphs 0072 and 0084 of this same patent publication describe one method to test the thermal stability of the polymerizable composition, and paragraph 0085 describes a method used to test the thermal stability of such compositions.

### Examples

The compositions tested contained 15 parts by weight of the organoborane/amine complex (with or without aluminum containing dopant) mixed with 70 parts by weight of an acrylic resin (comprised of 79 % methylmethacrylate, MMA, and 21 % of polymethylmethacrylate, PMMA, of 270 K Mw), 8 parts by weight of a polyoxyalkyleneamine (Jeffamine T403), 7 parts by weight of a Core-shell impact modifier (Paraloid EXL2691A) and 0.03 % by weight of an antioxidant (2,6-ditertbutyl-4-methyl phenol, BHT).

After the batches were properly mixed, they were placed in 8 oz. jars. The initial viscosity was measured with a Brookfield Digital Viscometer HATDV II, spindle #7 at 20 rpm. The jars were then placed in an oven set at 40°C, for the number of days indicated in the data. On the day that the viscosity was measured the samples were taken out of the oven and allowed to cool to room temperature, usually 4-6 hours. After the viscosity was measured, the samples were placed back in the oven. This procedure was repeated until the samples gelled.

Example	Borane	Amine	Al Source	Molar N:B Ratio	Molar B:Al Ratio	Pyrophoric	Days Under 100 kcPs
1	TNBB	MOPA	None	1.31	-	No	2.2
2	TNBB	MOPA	${}^n\text{Bu}_3\text{Al}_2(\text{OiPr})_3$	1.32	83.5	No	8.6
3	TNBB	MOPA	${}^n\text{Bu}_3\text{Al}_2(\text{OiPr})_3$	1.34	41.2	No	16.5
4	TNBB	MOPA	${}^n\text{Bu}_3\text{Al}_2(\text{OiPr})_3$	1.38	20.1	No	>19



What is Claimed:

1. A composition comprising an organoborane/amine complex and an effective amount of at least one organoaluminum compound to inhibit curing of the organoborane/amine complex when used as part of a polymerization initiator system containing olefinic unsaturation.
2. A composition as claimed in Claim 1 wherein the organoaluminum compound is of the formula  $Al_2R_6$ , with R being selected from the group consisting of  $C_1$ - $C_{12}$  alkyl and  $C_1$ - $C_{12}$  alkoxy and with each of the six R groups being the same or different.
3. A composition as claimed in either Claim 1 or Claim 2 having a molar ratio of boron to aluminum of from about 1.0:1.0 to about 50.0:1.0.
4. A composition as claimed in either Claim 1 or Claim 2 having a molar ratio of boron to aluminum of from about 10.0:1.0 to about 30.0:1.0.
5. A composition as claimed in any Claims 1 to 4 wherein the organoaluminum compound is one or more of trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, aluminum triethoxide, aluminum isopropoxide, aluminum tri-s-butoxide, aluminum tri-t-butoxide, diethylaluminum ethoxide, diisobutylaluminum ethoxide, triethyl(tri-s-butoxy)dialuminum, tri-n-butyl(triisopropoxy)dialuminum.

6. A composition as claimed in any Claims 1 to 5 wherein the organoaluminum compound was added to an organoborane prior to reaction with amine in preparing the organoborane/amine complex.

5        7. A composition as claimed in any Claims 1 to 5 wherein the organoaluminum compound was added to a preprepared organoborane/amine complex.

8. A polymerizable composition comprising one or more  
10 monomers, oligomers or polymers having olefinic unsaturation and, as the initiator system, the composition of any of Claims 1 to 7.